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ELECTRON-SURFACE INTERACTION AND METALLIZATION OF THE CaF_2 (111)-SURFACE STUDIED BY PHOTOTHERMAL TECHNIQUES

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The interaction of low energy electrons with the surface of alkaline-earth halides results in a variety of microscopical physical phenomena commonly described in terms of defect formation and diffusion, surface metallization and desorption of neutral- and charged particles. These processes are accompanied by local changes in the electronic and geometrical structure of bulk and surface and result in a variation of macroscopically measurable parameters like modulated optical reflectance and a deformation of the crystal lattice.

In this paper it will be shown that photothermal analysis, that so far has mostly been used for the determination of optical and thermophysical properties of materials, is also capable of measuring defect related nonthermal phenomena apparent during electron irradiation of insulator surfaces.

Experiments were performed with an intensity modulated electron beam of typically 1 μA at 1 keV focused into a spot of 1 mm^2 on the (111)-surface of a polished CaF_2 single crystal under ultra-high vacuum conditions.

Measurements revealed that modulated reflectance is sensitive to changes in optical properties induced by electron irradiation induced defects at low electron dosages. At a dosage level where metallization starts, a dramatic change in the modulated reflectance signal was observed indicating changes in electronic structure due to metal clustering at the surface.

The photothermal displacement technique has been utilized to monitor surface deformations induced by electron bombardment. It was found that results cannot be explained by a thermo-elastic expansion model that works well for metal surfaces. Therefore, this technique can be used for the measurement of nonthermal contributions to lattice expansion resulting from volume changes of created defects.

Keywords: defects, metallization, insulator surfaces, photothermal analysis, nonthermal processes.

1 INTRODUCTION

The interaction of energetic electrons with the CaF_2 (111)-surface has been studied experimentally by various authors. Early work concentrated on the identification of electron beam induced defects by their spectral characteristics.[1,2] Also the formation of colloidal particles by clustering of point defects has been investigated by spectroscopic means.[3] First results on the problem of a metallization of the surface can be found in the work of Strecker *et al.*[4] who measured changes in surface stoichiometry during electron irradiation by a variation of Auger line intensities. Later Saiki *et al.*[5] investigated electron beam-induced defect creation with much less electron dosages and identified defect related surface states by EELS.

The primary processes for the interaction of low energy electrons with alkaline-earth halides is the formation of electron/hole pairs (e/h pairs) where an energy of approximately 2.8 times the band gap energy is required to create one e/h pair.[6] The following processes have been studied extensively by ultrafast spectroscopy[7] and are now well understood. The creation of e/h-pairs leads to the formation of V_k centers with a certain mobility in the crystal lattice.[8] Within picoseconds these excitonic states are localized and form self-trapped excitons (STEs).[9]

The STE may either decay radiatively and thus restore the unperturbed lattice or separate into F-center and H-center lattice defects. The temperature dependent decay times of the STE luminescence in CaF_2 are well known and a radiative lifetime of 1.7 μs has been reported for room temperature;[7] i.e. the conditions relevant for experiments described in the present paper. Much less is known about recombination probabilities and diffusion properties of F- and H-centers. Early work on diffusion[10] yields only qualitative results on doped crystals while

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F- and H-center recombination in pure crystals has only been studied at low temperatures by Tanimura *et al.*[11] For the lifetime of F-centers at room temperature the authors present only speculative results and propose that stable lattice defects can only be formed by an additional hole excitation that may readily be provided by low energy electron excitation, however, with low efficiency. Also thermal activation of the separation process has been proposed.

In a certain temperature range F-center diffusion may result in the formation of colloids that are formed by an agglomeration of point defects.[3] H-center diffusion to the crystal surface is expected to result in the desorption of neutral fluorine. However, little is known about the accumulation of calcium at the surface that is expected from F-center diffusion to the surface, and the mobility of Ca atoms or clusters on the surface.

It is the intention of the present paper to address some of the open questions and to demonstrate how photothermal methods,[12] that so far have mostly been used for the determination of optical and thermophysical properties of materials, are also well suited for measuring defect related nonthermal phenomena apparent during electron irradiation of insulator surfaces.

The method of *modulated reflectance*[13,14] measures variations of the optical constants induced by a modulated source of electronic excitation[15] and can be used as an in-situ analytical tool for monitoring changes in the electronic structure at the surface. For the present investigation this method will be utilized for monitoring the development of a metallic surface layer and its band structure. The modulated reflectance response of a CaF_2 crystal containing F- and M-center defects will be derived via Kramers-Kronig analysis from the known absorption bands and it will be shown that metallization effects can clearly be separated from defect induced signals. A complete quantitative derivation of the modulated reflectance response, however, is beyond the scope of this paper since it requires better knowledge of the apparent band structure and the primary excitation processes.

The photothermal *surface displacement* technique[16] measures the deformation of a surface due to local thermoelastic expansion following modulated laser beam heating. In the present context the method is used to detect *non-thermal* contributions to the deformation of an electron irradiated CaF_2 surface resulting from expansion of lattice defects.

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2 EXPERIMENTAL

Measurements were performed on circular (8 mm$^{\varnothing}$ × 2 mm) IR-window grade CaF_2 single crystals from K. Korth company that were cleaved in the (111)-direction and then polished to obtain good optical quality. Surface roughness (mainly polishing scratches) could be estimated from AFM images to be approx. 50 nm.[17] Crystal temperature was controlled by a resistive heater element attached to the back side of the sample and a liquid nitrogen cooling device integrated into the copper sample holder. A temperature range of −80°C to +400°C could be covered, where heating and cooling rates had to be restricted to approximately 3 K/min to avoid thermal stress that would result in a destruction of the crystal.

All experiments were performed in ultra-high vacuum at base pressure of approximately $5 \cdot 10^{-10}$ mbar; after the first few measurements fluorine appeared to be the most abundant constituent of the residual gas.

The electron source was a standard 3 keV Auger electron gun providing typically 1.5 μA of 900 eV electrons focussed into a spot of 1 mm^2. The angle of incidence of 45° resulted in a considerably large inhomogeneity of the current density over the elliptical beam profile on the sample surface. Electron beam chopping for modulated measurements was accomplished by a square wave voltage with a frequency of 100 Hz to 10 kHz applied to the beam deflection plates of the electron source.

Static reflectivity was measured utilizing the beam of a 1 mW single mode HeNe laser that was focussed onto the sample surface. The reflected light was analyzed with a power meter.

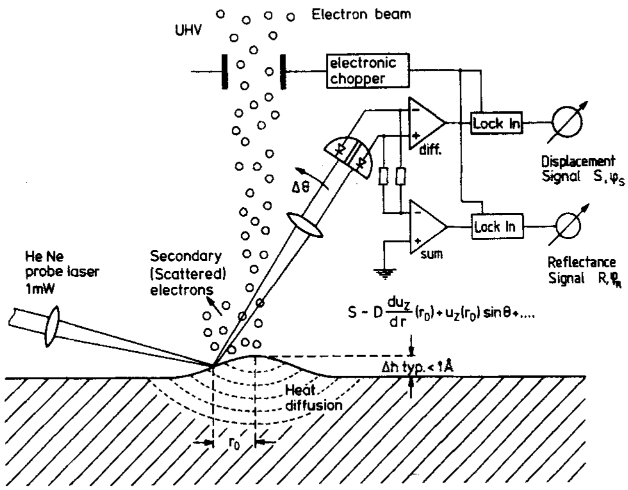

FIGURE 1 Schematic of the experimental setup used for modulated reflectance and surface displacement measurements with electron excitation.

A schematic of the experimental setup used for modulated reflectance and surface displacement measurements is shown in Figure 1. The surface was probed by the same HeNe laser used for the static reflectivity measurements, however, the reflected beam intensity was measured by a fast quadrant detector coupled to lock-in amplifiers that were synchronized to the electron beam chopping frequency.

For modulated reflectance operation signals from all quadrants of the photodetector were added and thus the modulated part of the surface reflectivity was measured. For a measurement of the modulated surface displacement, signals from quadrants opposite to each other were subtracted in the preamplifiers of the lock-in detectors to obtain the angular deflection of the probe beam in x_d and y_d directions, respectively (see Figure 2).

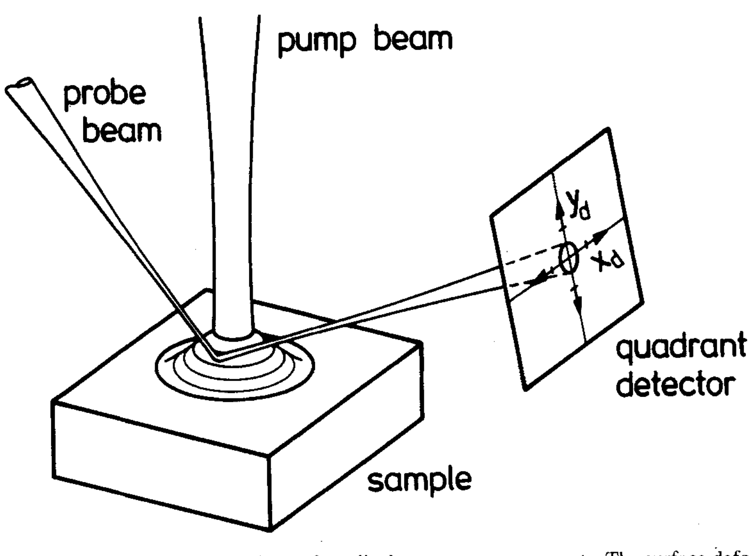

FIGURE 2 Probe laser beam geometry for surface displacement measurements. The surface deformation is probed by measuring the displacements x_d and y_d of the probe beam with a quadrant photodetector.

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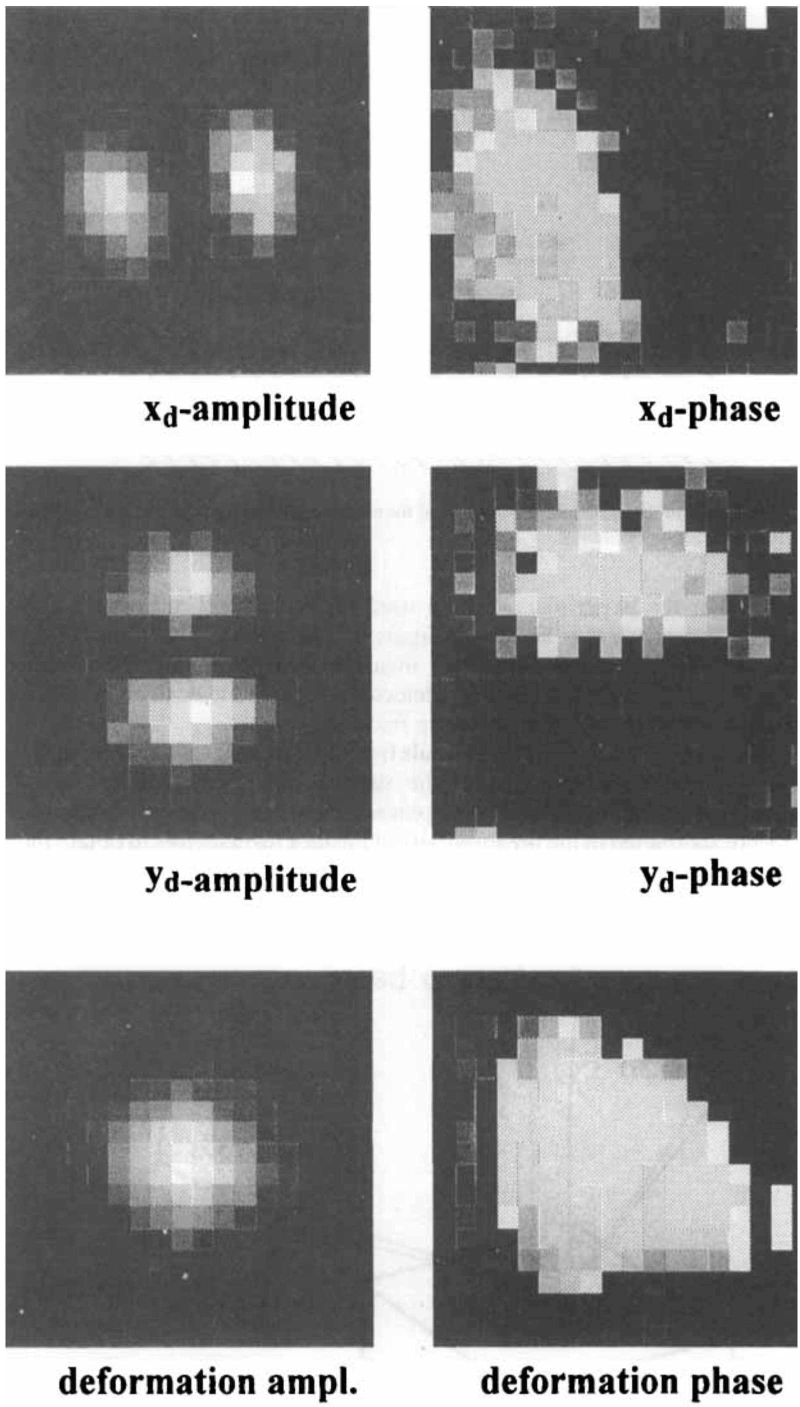

FIGURE 3 Amplitude (lower left) and phase (lower right) of the electron beam induced surface deformation are reconstructed from the displacements x_d and y_d (upper figures) by a numerical integration over the scanned region.

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Two-dimensional images of the spatial derivatives of the surface deformation were obtained by scanning the electron beam relative to the position of the probe beam focus on the crystal surface. Typical examples for amplitude and phase of the x and y derivatives are shown in the upper part of Figure 3. The contour and phase plot of the surface deformation u_z was obtained by a geometry corrected integration of complex arrays containing the deflection data $x_d(x,y)$, $y_d(x,y)$ as a function of the surface coordinates x and y. Since the deflections of the probe beam are small, amplitude S and phase Φ of the surface deformation can be obtained by a simple first order approximation for a deformation profile with radial symmetry:[18]

$$S(r) = |u_z(r)| \quad \Phi(r) = \arg[u_z(r)] \qquad \text{where}: u_z(r)\, N \int_0^r \sqrt{x_d^2(r) + y_d^2(r)\, sin^2\, \Gamma}$$

Here $r = (x^2 + y^2)^{-1/2}$ is the radial coordinate, Γ the angle between the sample surface and the reflected probe beam and N is a normalization constant depending on the detector sensitivity. The result of such an integration is shown in the lower part of Figure 3. The phase image represents a radial distribution with increasing phase lag for increasing radial distance from the center of the excitation. At distances far away from the center a constant phase value indicates mechanical coupling of the elastic surface to the excitation region.[16] The amplitude image represents the bell shaped distribution of displacement height and is characterized by the maximum value in the center and the $1/e^2$ width of the radial distribution. Amplitude values are corrected for changes in static surface reflectivity occuring during the scan.

3 MODULATED REFLECTANCE

Previously it had been shown that the irradiation of the CaF_2 surface with electrons of energy and current density as described in the present paper results in a strongly temperature dependent surface metallization that can not only be detected by a rise in static reflectivity but also results in a significant change in the modulated reflectance response of the surface.[19] The latter phenomenon was attributed to the formation of Ca clusters on the surface and the formation of a metallic band structure interacting with the probe laser light. Later, direct evidence for surface clustering has been given by atomic force microscopy.[20] In the following some basic aspects of modulated reflectance signal generation in a halide crystal are outlined and then experimental results are discussed along the guidelines of the model.

Since a low intensity laser beam with a photon energy of 2 eV (633 nm) cannot interact with a 12.8 eV bandgap dielectric, no modulated reflectance response can be expected from a pure CaF_2 crystal and any thermoreflectance response from the crystal itself can be excluded for all measurements presented here. However, as soon as electron induced defect states are present that have absorption bands in the visible spectral region, optical constants for the HeNe laser light are changed and a modulated reflectance signal is expected, provided the defects are created and decay during the chopper period. Under these circumstances two different physical qualities can be derived from modulated reflectance measurements performed on a CaF_2 crystal not yet metallized. The *spectral behaviour* of the modulated reflectance signal should resemble the optical properties of the defect states while the *dynamical response* (i.e. frequency dependence in modulated experiments) yields information about lifetime and diffusion properties of the defects.

A prediction of the defect induced change in reflectivity at a CaF_2 surface may be obtained by the following model that assumes an absorption by F- and M-center defects as observed

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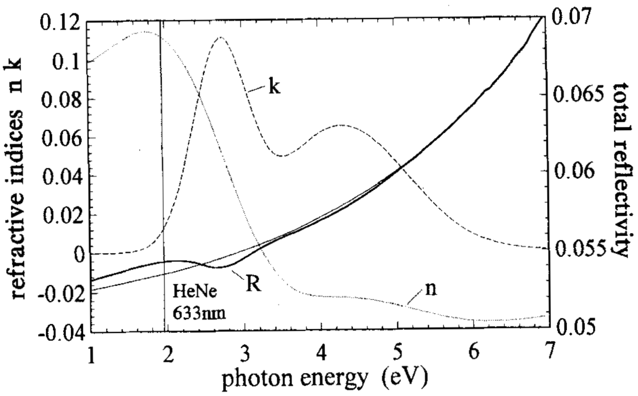

FIGURE 4 Photon energy dependent reflectivity of a CaF_2 surface with (thick solid curve) and without (thin solid curve) F- and M-center defects. Reflectivity was calculated from the real (n) and imaginary (k) part of the complex index of refraction for an angle of incidence of 35° with the respect to the surface normal.

in electron irradiation experiments. The wavelength dependent absorption of these defects taken from the literature[7] exhibits two pronounced absorption peaks at 2.7 eV and 4.3 eV and is represented in Figure 4 as a dashed curve. The absorption spectrum is fitted by a sum of two Gaussian absorption lines, and the real part n of the complex index of refraction is derived from a Kramers-Kroning analysis and represented as a dotted line in Figure 4. Taking into account the refractive index of CaF_2 over the relevant spectral region,[21] the total reflectivity is calculated (thick solid curve). As the absolute concentration of defects and their distribution is presently not known for the irradiation experiments, results for the reflectivity are only qualitative and allow a decision about the sign of the modulated reflectance signal from Figure 4 but not about the absolute magnitude. In the present calculation the change of reflectivity induced by the defects is positive for low photon energies and negative for high energies and the crossover occurs at about 2.4 eV. Therefore, a positive modulated reflectance signal is expected for the HeNe laser light at 633 nm.

Modulated reflectance measurements were performed in two different ways. While irradiating continuously the signal was either recorded as a function of the slowly varied crystal temperature or for various constant temperatures as a function of the irradiation time.

A measurement of the first type covering the temperature range of –80°C to +300°C is shown in Figure 5. In this figure the temperature dependence of the static reflectivity is included as a reference. The reflectivity curve indicates a weak metallization for temperatures below 100°C and a significant rise of the metallization rate up to 200°C. At higher temperatures the rate increases even more, however, the metal coverage of the surface is drastically reduced by thermally stimulated desorption of Ca. Consequently, virtually no metallization is found for temperatures above 250°C.

The modulated reflectance response is directly correlated with this development. In the temperature region of low metallization (up to 60°C) a positive, nearly constant signal indicates that modulated reflectance is dominated by electron induced defect creation. The origin of the initial rise between –80°C and –30°C is not yet clear; speculative interpretations may include defect accumulation or experimental artefacts like charging effects.

A dramatic decrease and a change in sign of the signal is observed in a narrow temperature interval between 60°C and 120°C that can be attributed to the formation of metallic clusters on the crystal surface. The electronic structure of small agglomerates changes rapidly during the formation process resulting in strong variations of the optical response to the probe laser light.

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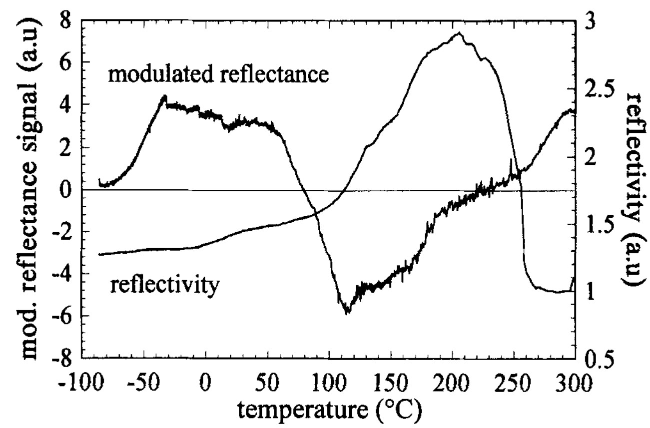

FIGURE 5 Temperature dependent modulated reflectance signal (1.2 kHz modulation frequency) at 633 nm for an electron irradiated CaF_2 surface. The second curve represents the static reflectivity measured simultaneously.

As will be demonstrated below the amplitude of the modulated reflectance signal is not only a function of temperature but also subject to changes depending on irradiation time; e.g. the signal rises if a certain irradiation dose is exceeded. This may readily explain the increase in modulated reflectance signal observed above 120°C. Additionally, the rising temperature may mediate the formation of larger clusters and thus contribute to variations in modulated reflectance. Additionally, thermally stimulated desorption of Ca has to be taken into account for temperatures higher than 170°C. Above 230°C the Ca layer is gradually depleted and the signal changes its sign again. At 300°C where static reflectivity indicates a complete removal of the metallization layer, the modulated reflectance recovers the positive low temperature value typical for the irradiated but non-metallized CaF_2 surface.

The development of modulated reflectance with electron dosage for various constant temperatures is shown in Figure 6. The general trend for all curves is a decrease of the signal followed by a change in sign after 1 to 2 minutes irradiation time. After passing a temperature dependent minimum the signal slowly recovers and exhibits a tendency towards

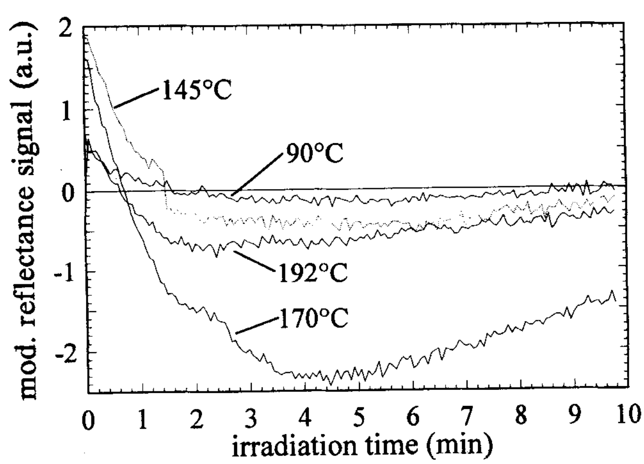

FIGURE 6 Development of the modulated reflectance signal at 633 nm with electron dosage for various crystal temperatures.

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zero for long irradiation times. This implies that high reflectance amplitude values obtained by irradiation at high temperatures (high metallization rate) cannot be obtained at lower temperatures even for very long irradiation times. Since the modulated reflectance response is determined by the size and shape distribution of Ca clusters on the surface it can be concluded that these distributions are not simple functions of the electron dosage or average metal coverage but depend on a complicated interplay between metal production and desorption with surface diffusion and amalgamation of clusters. As all these processes strongly depend on the crystal temperature, irradiation at a specific temperature leads to a unique result for the apparent surface electronic structure.

Due to the complicated physical structure and surface interaction of the Ca clusters a theoretical prediction of their modulated reflectance response is impossible at the present stage, however, a correlation of modulated reflectance results with surface morphology as determined by atomic force microscopy and additional spectroscopic information will provide at least a phenomenological understanding of the reflectance signals. Therefore, modulated reflectance is a very promising tool for an optical in-situ determination of surface electronic properties of metallized surfaces.

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4 SURFACE DISPLACEMENT

The method of modulated surface displacement[16] is well established for the measurement of optical and thermal properties of bulk and thin film materials. Recently the usage of this technique has been extended to the measurement of surface displacements induced by modulated electron beam heating.[22,23]

In the present paper the surface displacement technique is utilized for the detection of *non-thermal* defect induced processes at the CaF_2 surface. It has been predicted theoretically that the volume taken by STE or F-center defects in a halide crystal is larger than that of the constituent of the unperturbed lattice.[24,25] Such an effect has been investigated in KBr by measuring transient defect induced stress resulting from pulsed electron irradiation.[26] This was accomplished by monitoring the rotation of the polarization of a probe laser beam passing regions with a stress gradient. As a disadvantage of this method, however, it should be mentioned that the probe beam might also interact optically with the crystal defects and thus a rotation of the polarization may also result from optical excitation of defects.

On the contrary, the surface displacement technique offers a direct method for the observation of a defect induced local expansion of the crystal. Any changes in optical constants of the crystal that might influence the reflection of the probe beam can be compensated by proper normalization, provided, the probe beam is tightly focussed and thus is a local probe of regions with small inhomogeneity.

To detect and separate nonthermal contributions to the surface displacement signal for electron irradiated CaF_2, amplitude and phase of the displacement signal were recorded as a function of the modulation frequency at room temperature and as a function of the temperature at a fixed frequency of 1.2 kHz. For each data point a two-dimensional scan was taken and displacement signals were converted to the deformation profiles according to the algortithm described above.

The theoretical dependence of height and width of the surface deformation as well as the phase in the center were calculated from a thermal transport model based on the solution of the heat diffusion equation for the appropriate boundary conditions.[27] This model yields the temperature field $T(r,z)$ in a bulk material subject to modulated electron irradiation. Subsequently the surface displacement $u_z(r,0)$ was calculated by integrating over contributions from all regions up to a critical depth z_0 determined by the penetration depth of the heat wave:

$$u_z(r,0) = \alpha_{th} \frac{1+\nu}{1-\nu} \int_0^{z_0} T(r,z)\, dz$$

Here r and z denote the radial and depth coordinates while α_{th} and ν represent the coefficients of thermal expansion and the Poisson number of the material, respectively. It has been shown that for the relevant experimental conditions (i.e. electron beam diameter is much larger than thermal diffusion length) this model yields accurate results, although, the simplified one-dimensional integration neglects any shear effects in the thermoelastic response.[28] Since it covers all relevant thermal contributions to the surface displacement any deviation of experimental results from curves calculated with this theory indicate that non-thermal effects contribute to the surface deformation.

A typical frequency response curve of the deformation height for CaF_2 calculated assuming an electron beam diameter of 1 mm is shown as a solid curve in Figure 7. Since there is considerably large uncertainty about the electron beam diameter apparent during measurements the calculation has been repeated for diameters 20% smaller and larger than the nominal value. Results for these diameter values are shown as dotted lines. The calculated amplitude falls monotoneously with frequency and exhibits a saturation behaviour for low frequencies that is typical for a surface absorber where the thermally active volume is controlled by the diffusion length rather than by the excitation volume. In the frequency range 100 Hz–10 kHz (that is presently accessible for measurements) the amplitude varies by less than one order of magnitude.

Figure 7 also displays experimental data (triangles) obtained for the same beam diameter as used for the calculation. A striking discrepancy between theoretical and experimental curves is immediately apparent. Experimental data exhibits a $1/f$-dependency of the amplitude on modulation frequency. Only a slight tendency towards saturation at low frequencies might be deduced from the curve by a very careful data analysis. This functional behaviour for the amplitude is typical for a situation where the signal is not influenced by diffusion and, therefore, the active volume is independent of frequency.[29] Since the calculation clearly shows a dependence of the displacement signal from thermal diffusion,

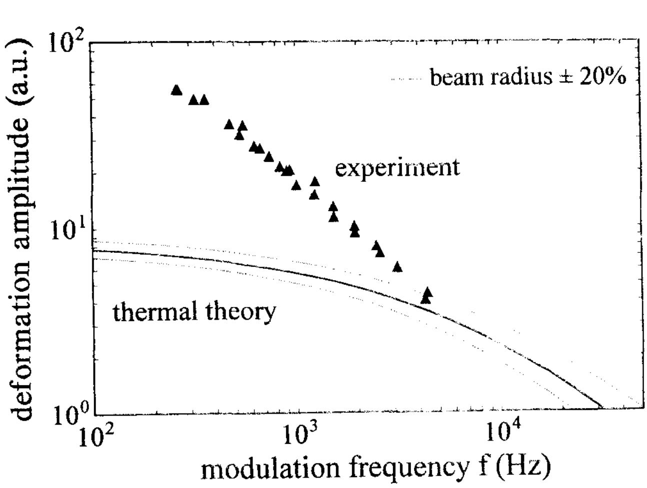

FIGURE 7 Surface deformation height of electron irradiated CaF_2 as a function of the electron beam modulation frequency f. Triangles represent measured values while solid and dashed curves are result of a theoretical calculation based on a pure thermoelastic expansion model.

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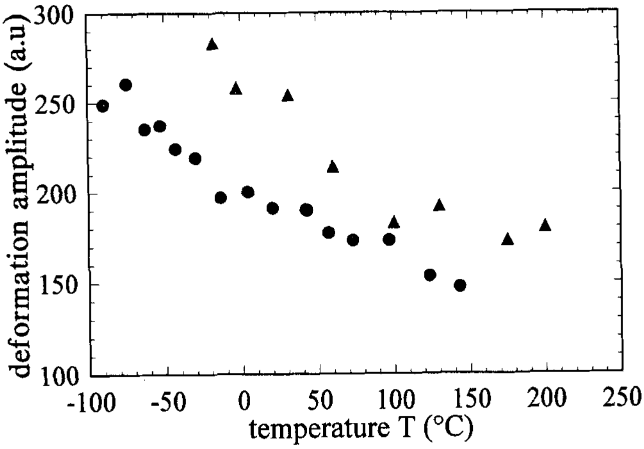

FIGURE 8 Temperature dependence of the deformation height for an electron irradiated CaF_2 surface for a modulation frequency of 1.2 kHz. The two sets of data represent results from measurements at two different locations on the crystal surface.

experimental data may consistently only be interpreted on the assumption of non-thermal contributions to the surface displacement; i.e. creation and decay of defects during the modulation period results in a local expansion of the lattice. A qualitative conclusion that can be drawn from the observed $1/f$-behaviour is that the defect diffusivity must be much lower than the thermal diffusivity.

For a further confirmation of the non-thermal character of the displacement signal observed in electron irradiated CaF_2 crystals the temperature dependence of the surface deformation has been investigated. The height amplitude of the surface deformation at a frequency of 1.2 kHz was measured over the temperature interval from −80°C to +300°C. Results of measurements at two different locations of the crystal surface are shown in Figure 8. Due to temporary optical missalignment arising from thermal stress during sample heating results of successive scans are not completely reproducible. However, as a consistent result of several scans it was found that the deformation amplitude falls monotoneously with rising temperature.

Assuming a purely thermal origin for the surface displacement any temperature dependence can only be a result of changes in thermoelastic constants. An analysis of the dependence of the surface displacement as a function of these constants yields:[16]

$$u_z \propto \frac{\alpha_{th}}{\kappa} f(D_{th})$$

where α_{th} is the coefficient of thermal expansion while κ and D_{th} denote thermal conductivity and thermal diffusivity, respectively. The function $f(D_{th})$ is a complicated integral function of the thermal diffusivity, however, from simple physical considerations it is obvious that the surface deformation u_z will be lowered if the thermal diffusivity D_{th} rises.

The temperature dependence of α_{th}, κ and D_{th} as found in the literature[30,31] is depicted in Figure 9. While the thermal expansion increases monotoneously with temperature the latter two quantities have a negative temperature coefficient. Therefore, from a thermal model a decreasing surface displacement would be expected when increasing crystal temperature, what again is opposite to the experimental observation. The decreasing displacement signal cannot be explained quantitatively at the present stage, however, the measured temperature

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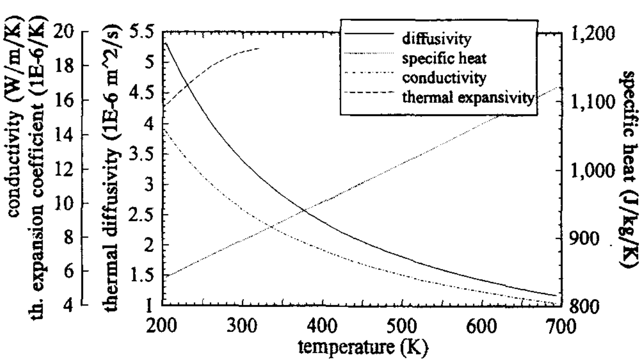

FIGURE 9 Temperature dependence of thermal and thermoelastic parameters of CaF_2 as found in the literature. The temperature dependent curves have been calculated from room temperature data (Ref. 31) using standard models of solid state theory from Ref. 32.

dependence yields additional evidence that the displacement signal is not solely governed by thermal expansion but strong non-thermal contributions play a major role.

5 CONCLUSIONS

Two different phenomena occuring during electron irradiation of CaF_2 have been investigated by photothermal techniques namely changes in electronic structure during Ca clustering at the surface and a non-thermal surface deformation due to electron beam induced defect creation. Both types of measurements are based on simple UHV compatible probe beam techniques and have the capability to be used as in-situ methods for the inspection of surface properties of dielectrics subject to defect creating radiation. Presently these methods may be used for a qualitative understanding of surface processes. Work for a quantification of these results and an absolute calibration of the techniques is in progress.

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